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GLYCERIDES

By GEORGE Y. BROKAW*

While many types of "glycerides" exist, the term will be restricted here to mean aliphatic esters of glycerol. These are referred to as triglycerides (fully esterified), diglycerides, and monoglycerides, depending upon the number of fatty acid radicals in each molecule. *Chemical Abstracts* uses α, β, and γ to indicate the position of attachment of a substituent on glycerol unless glycerol is called 1,2,3-propanetriol, in which case the position of a substituent is indicated by the appropriate number. This author prefers a common alternative of 1, 2, and 3 with glycerol to avoid confusion with the Greek letters α, β, and β' which are used to designate polymorphic crystalline forms of the glycerides.

Triglycerides are the main components of fats and oils and their behavior is extremely important to a wide variety of industries. In spite of this, and of the fact that fats and oils were some of the early substances to be investigated chemically, a good understanding of glyceride chemistry has begun to develop only in relatively recent years. For detailed treatment of certain aspects of glyceride behavior, the reports of a seminar held in 1941 (1) are invaluable.

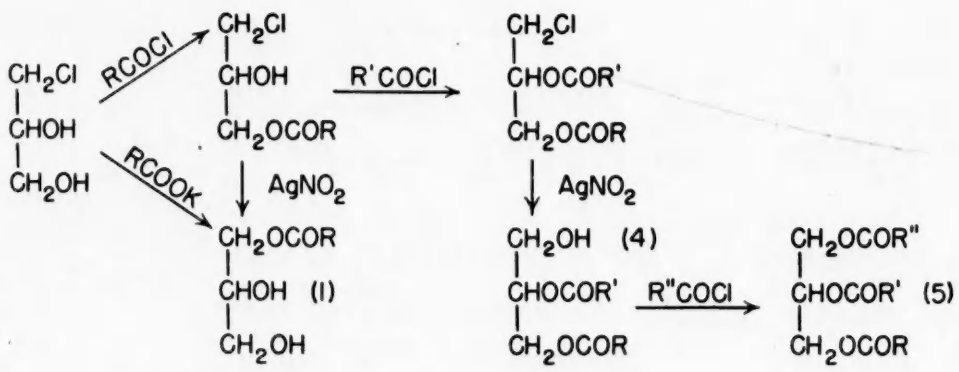
Synthetic Methods

An understanding of the ester chemistry involved in glycerides is easily approached by a review of the procedures used to synthesize specific compounds. These procedures are applicable for preparing mono-, di-, and triglycerides, and they are presented in the order in which they were discovered.

In the period 1900-1920, Grün (2) proposed a synthetic scheme based on the chlorohydrins, as shown in Chart I. Grün failed to recognize the isomerization pos-

CHART I

Grün's Synthetic Methods



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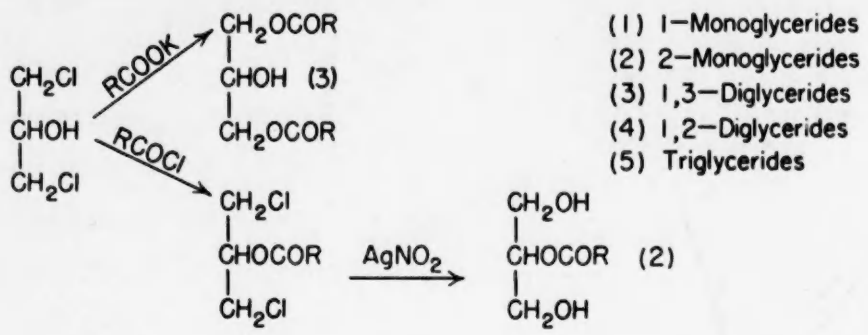
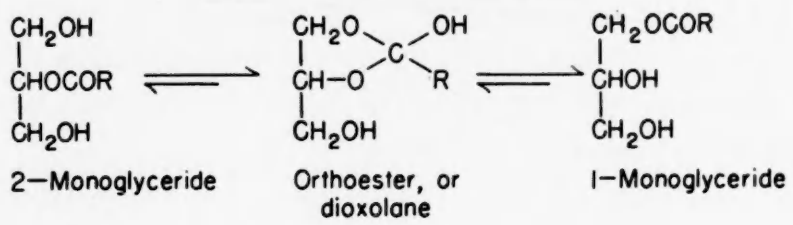


sibilities in his raw materials and in the intermediates, especially during reaction. As a result, he may have prepared pure 1-monoglycerides and 1,3-diglycerides (only where R = R′), but other compounds were probably quite impure.

This became evident in 1920 when Emil Fischer (3) showed that 1-monoglycerides were far more stable than the 2-isomers, and proposed a mechanism for the isomerization of the latter (Chart II).

CHART II

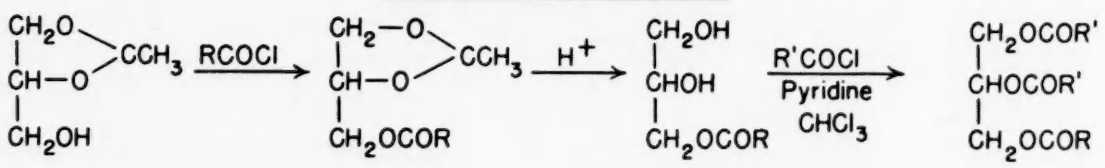
Fischer's Isomerization Mechanism



Fischer also developed a synthetic procedure for making certain authentic glycerides. This procedure was based on two factors which he proved: (1) acetone condenses with glycerol to form exclusively a 5-membered ketal ring; and (2) reaction of an acyl halide with a partial ester in the presence of pyridine and chloroform results in no isomerization.

CHART III

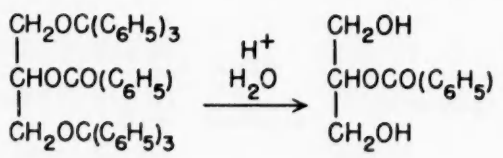
Fischer's Synthetic Method



(No isomerization)

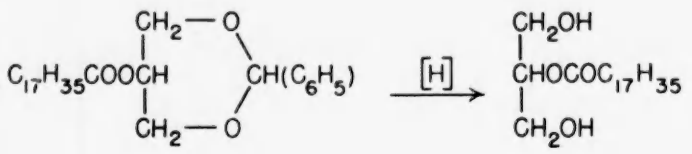
However, 2-monoglycerides still were not available, and synthetic methods were incomplete for other glycerides. Grün recognized Fischer's contribution, but many other workers did not, and, as a result, the literature of 1920-1929 contains many incorrect preparations.

Helferich and Sieber (4) made the first 2-monoglycerides (aromatic) by the acid hydrolysis of 1,3-dityrityl-glycerol-2-monobenzoate.



This was possible only because of the decreased migratory tendency of the aromatic ester. The procedure was not applicable to aliphatic glycerides.

Bergmann and Carter (5) prepared 1,3-benzylidene-2-monostearin and hydrogenolyzed it to make the first aliphatic 2-monoglyceride (2-monostearin). This method was successful, again because of two factors: (1) in contrast to acetone,

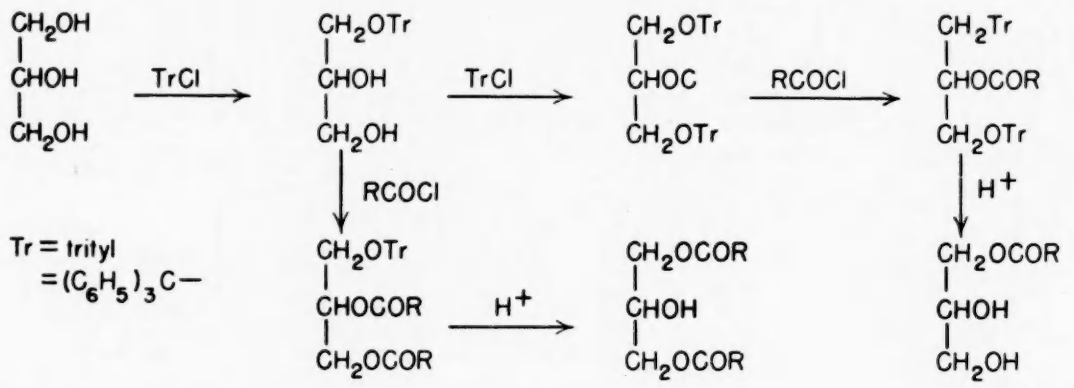


benzaldehyde forms a 6-membered ring with glycerol; and (2) absolutely acid-free catalyst is necessary in the hydrogenolysis to insure a lack of isomerization.

Verkade (6) used a scheme which became applicable to all glyceride syntheses (Chart IV).

CHART IV

Verkade's Synthetic Method

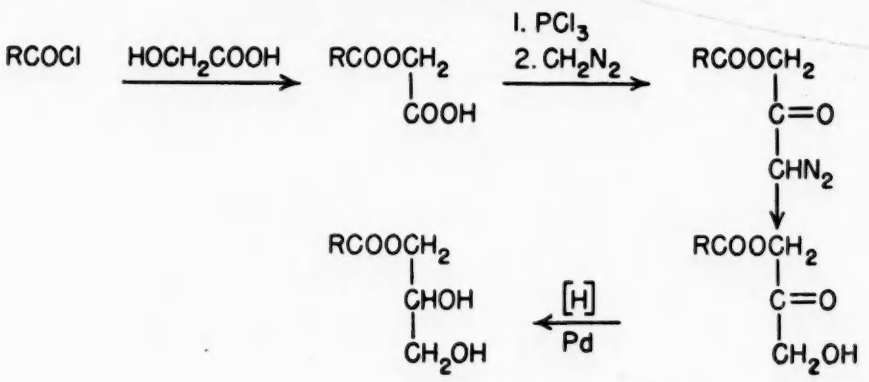


This method is dependent upon quantitative migration of 2-acyl groups to the 1-position, as shown. He proposed, based on the findings of Bergmann and Carter, that hydrogenolysis would avoid the isomerization where preferred and that this would complete the scheme. This was later confirmed.

Most preparations of pure glycerides are now carried out, using Verkade's scheme or the equivalent benzylidene glycerol route. A very recent innovation is to build the glycerol molecule after forming the ester link, thus obtaining a 1-monoglyceride. The method of Schlenk (7) is illustrated in Chart V. This last attack is useful in radioactive labeling of a known carbon atom of glycerol for tracer studies on glycerides.

CHART V

Schlenk's Monoglyceride Synthesis



Polymorphism

Identification of pure compounds by their melting points has been severely handicapped by the existence of several crystalline forms for most glycerides. Duffy, in 1852, first obtained a natural fat fraction by solvent crystallization which showed three distinct melting points, now recognized as the values for the three forms of tristearin. The significance was not recognized until much later, and only very recently have Malkin (8), Lutton (9), and others made a true science of this feature by x-ray diffraction work. The effect of polymorphism on melting point is illustrated in Table I.

Table I. Melting Points of the Crystalline Forms of Glycerol Stearates

	β	β'	α	sub α
1–Monostearin	81.5	78	74	49
2–Monostearin	74.5	*	*	*
1,3–Distearin	78.2**	*	*	*
Tristearin	73.1	64	54.9	*

*Nonexistent, according to the latest data.
**Beta-b = 78.2; beta-a probably 77.2.

Since polymorphism affects physical properties even more in some instances than chemical differences, its importance in fat and oil technology can be visualized. For example, it is one of several complex factors (10) responsible for the tempering of fats. Tempering is the process of inducing consistency changes in freshly solidified fat *via* crystal modification by holding it at a specified (usually slightly warm) temperature. Since cocoa butter is particularly susceptible to polymorphic existence, chocolate technology is quite complex.

Optical Activity

If the groups attached to the two end carbons of glycerol are different, optical activity can exist. Fischer and Baer (11) have developed synthetic procedures based on *d*-glyceraldehyde. By using Emil Fischer's esterification technique with or without blocking of the primary hydroxyl group, followed by controlled hydrogenation, optically active partial esters are obtained. Esterification then gives triglycerides. Only the partial esters show rotatory power unless one of the acid groups is aromatic. The magnitude of rotatory power is small and decreases with increased molecular weight (*d*-1-monostearin has $[\alpha]_D^{25}$ of $-3.86°C$ in pyridine). By ingenious synthetic routes, complete retention of rotatory power was proved for all chemical steps involved.

Industrial Monoglycerides

Glycerol can be reacted with triglycerides to give monoglycerides and diglycerides. All four isomeric species exist in random distribution, as determined by the mass action principle. This reaction has been used for some time to produce partial ester products for many purposes, including emulsifiers for use in food products. Until recently, all such products were mixed esters because of the inability to separate the desired monoglycerides without reversion of the reaction. Selective crystallization simultaneously with reaction from a mutual solvent has been

effected in the laboratory; in this way, pure 1-monostearin has been prepared from tristearin. Molecular distillation now permits the attainment of monoesters of at least 90% purity on a production scale.

Ester-Ester Interchange

Ester-ester interchange is more difficult to achieve than alcoholysis. Extremely alkaline materials, such as sodium methoxide, will catalyze this reaction at low temperatures, and this is becoming important industrially. The fatty acids may be randomized in a nonrandom fat, this change affecting utilization. For example, lard is improved greatly as a shortening by this treatment. This reaction also can be used to precipitate saturated glycerides from mixed fats, for example, tristearin from oleostearins.

Miscellaneous Fat Chemistry

For many decades, glycerides have been saponified with alkali to produce glycerol and soap, and they have been boiled with water in the presence of sulfonic acids (Twitchell's reagent) to yield glycerol and fatty acids. High-temperature and high-pressure continuous countercurrent hydrolysis is rapidly being introduced as the most satisfactory industrial fat-splitting procedure. At about 260°C and 900 pounds per square inch, the reaction takes place without added catalyst.

Other important industrial reactions of glycerides include that with ammonia to produce amides and amines. Beauvault-Blanc reduction (sodium and alcohol) is used to make fatty alcohols which can also be produced by catalytic hydrogenation.

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A MICROMETHOD FOR THE DETERMINATION OF ETHYLENEDIAMINETETRACETIC ACID (EDTA)

By C. H. ZUEHLKE*

Only a few methods are available for the determination of microamounts of ethylenediaminetetracetic acid (EDTA). Perhaps the most useful of these described by Darbey (1) is based on the use of nickel as an "indicator" ion. The excess nickel is removed by dimethylglyoxime and the amount of nickel-EDTA complex formed is determined by the dithiooxalate method.

A somewhat similar method which utilizes cobalt as an indicator ion has been successfully applied in these Laboratories. The sample solution is reduced to a volume of 1 milliliter and is treated in a separatory funnel with 500 milligrams of

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solid ammonium thiocyanate, 20 mg of anhydrous trisodium phosphate, and 0.20 ml of 0.0005 *M* cobalt nitrate solution. The resulting solution is extracted with 10 ml of 1:1 (*v*/*v*) isoamyl alcohol-ethyl ether previously saturated with water. The absorbance of this solution is read in a 10-cm cell at 620 millimicrons.

In the absence of EDTA, cobalt is quantitatively extracted by the organic phase. By forming a stable complex, EDTA decreases the amount of cobalt extracted, and consequently decreases the color intensity of the organic solution. A calibration curve, prepared by using known amounts of EDTA, is a straight line up to 74 micrograms. By increasing the amount of cobalt used, the range of the method probably can be extended considerably, with a proportionate decrease in sensitivity.

Cobalt, like nickel, will displace most of the commonly encountered metals from their EDTA complexes. The method, therefore, in most cases, will determine complexed as well as uncomplexed EDTA. Since copper and nickel also form very stable complexes, these metals are likely to compete successfully with cobalt for the EDTA present. The interference of iron is prevented by the addition of phosphate. Under the conditions of the test, as much as 400 μg of citric acid does not interfere.

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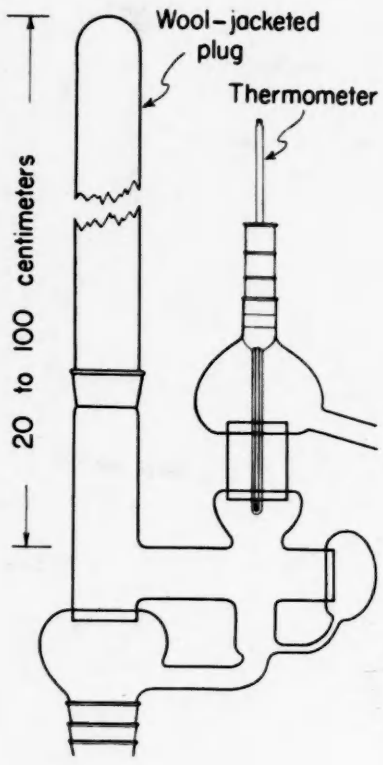

A Still-Head

A still-head found most useful for distilling, at high temperatures and with high capacity, materials which tend to bump or creep, is described. The antibump feature is a closed straight tube the same diameter as the neck of the flask and attached on the same axis as the neck. It does not prevent bumping, but it does cushion the violence of the bump and allows the liquid to flow back into the distilling flask instead of the receiver.

The high capacity is achieved by collecting the products of flooding, creep, and entrainment and returning them to the flask *via* a tube separate from the vapor path. Entrainment is reduced by allowing the liquid to impinge on the target and conducting it back to the flask. Creeping is prevented by the pear-shaped annular rings, one located immediately above the neck of the flask and the other near the thermometer bulb.